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(54) A method and plant for removing pollutants from a combustion gas

Verfahren und Vorrichtung zur Abscheidung von Verunreinigungen aus einem Verbrennungsgas

Procédé et dispositif pour enlever des polluants à partir d'un gaz de combustion

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Description

The present invention concerns a method for removing pollutants from a combustion gas of post-combustion type, in particular, for removing sulphur dioxide (SO_2) and nitroges oxides (NO_x).

Generally, in said types of method the removal of sulphur dioxide occurs by means of thermo-chemical reactions, even in the absence of energy transfer to the gas, and radical reactions in the presence of energy transfer to the gas.

There are noted post-combustion methods, some of which apply the technology of selective catalytic reduction of nitrogen oxides by means of the injection of ammonia (NH_3) and others remove nitrogen and sulphur oxides by means of energy transfer to the combustion gas; with the latter methods , in general, first an interaction between the gas and electrons of appropriate energy is caused in order to transform the sulphur dioxide and nitrogen oxide respectively into sulphuric acid (H_2SO_4) and nitric acid (HNO_3), then there is an intake of ammonia to reduce said acids to ammonia salts and lastly a removal of said salts in an electrostatic precipitator and/or Bag Filter system.

The methods cited above offer a good degree of reduction of nitrogen oxides but bear the disadvantages of high costs, limited duration, leakage of ammonia into the atmosphere and high load losses in the gas circuit. There are also noted post-combustion wet "scrubber" methods which present the difficulty of discharging the solution and/or the sludge containing sulphates and nitrates and the necessity of heating the combustion gas before passing it into the atmosphere.

A new technology, called Plasma Induced DeNOx, DeSOx, able to remove principally nitrogen and sulfur oxides based on gas energization, is under development in several laboratories since 1985. In this technology free electrons having energy in the range 4 20eV are produced by applying very short pulse voltage (200 1000 nsec) to a stressed electrode structure like wire-plate or wire-cylinder. The free electrons so produced dissociate part of water and oxygen molecules present in the gas and free radicals are produced. The radicals convert about 10 20% of SO_2 present in the gas into sulfuric acid; convert about 70% of NO into NO_2 and remove about 20% of NOx. In this process ammonia is added to the gas in order to convert the acids produced into the ammonium salts, remove SO_2 via thermochemical reaction and increase the NOx remotion by hetereogeneous reactions.

In the Plasma Induced DeNOx DeSOx tehchnology, the largest part of SO_2 is removed by thermochemical reaction among ammonia, SO_2, H_2O and O_2; this reaction is spontaneous and its velocity increases as the temperature of the gas decreases. By this reaction SO_2 is converted principally into neutral Ammonia sulphate and acid Ammonia sulphate. The formation of the acid Ammonia sulphate is a great problem because not all the ammonia added to the flue gas reacts and a large concentration of NH_3 (hundreds of ppmv) is present at the outlet of the process. This drawback can not be solved reducing the quantity of ammonia injected, but the leakage of NH_3 can be reduced (tens of ppmv) by installing a bag filter at the end of the process. Due to the phisycal behaviour of ammonia salts (sticky) the bag filter clogs rapidly and maintenance problems rise from an industrial point of view.

In the following description the "combustion gas" is referred to sipmly as "gas".

The invented method, as characterised in the claim , obviates the greater part of the above cited drawbacks; for instance, the ammonia leakage disappears.

The method comprises in sequence the phases of:

a) intake of the gas and cooling it to about 110°C with atomised water in at least one first cooling chamber or in the gas transport duct,

b) removing up to around 90% of the light ashes present in the gas in at least a first electrostatic precipitator,

c) further cooling of the gas to bring the temperature to about 80°C,

d) in at least one reaction chamber, in which dry ammonia is added to the gas, at the same time energising the gas by means of voltage pulses so as to produce the radicals in the gas and consequently the radical reactions necessary for the removal of part of the nitrogen and sulphur oxides;

the following phases e), f) being the ones that characterize the invention:

e) maintaining the temperature of the gas in said at least one reaction chamber at about 100°C in order to reduce the thermo-chemical conversion of sulphur dioxide to partially acidic sulphites and sulphates.

f) in at least one injection chamber, injecting a solution of hydorgen peroxide into the gas to convert the sulphur dioxide residue into sulphuric acid which reacts with the ammonia producing ammonium sulphate; the concentration of hydrogen peroxide in the fumes stays in the region of 0.7 times the concentration of the SO_2 present at the entrance of the plant;

g) in at least one second electrostatic precipitator, retain said ammonium sulphate;

h) possibly, in at least one filtration chamber, equipped with suitable filtres, cause chemical reactions in heterogeneous phase to improve the removal of nitrogen oxides.

A plant adapted to put the method into practice comprises:

i) a cooling chamber provided with means to inject atomised water into the gas in transit in order to lower the temperature of the gas to about 110°C;

ii) at least a first electrostatic precipitator to remove up to 90% of the light ashes from the gas in transit;

iii) a cooling chamber to lower the temperature of the gas to about 80°C;

iv) at least one reaction chamber that is similar to a wired plate electrostatic precipitator, this being supplied with a positive impulsive voltage of adjustable repetition frequency, and being provided with means to inject dry ammonia into the gas in transit; inside the reaction chamber the radicals necessary for the conversion of the nitrogen and sulphur oxides are produced by means of electrons generated by the impulsive electric fields; owing to the temperature of the gas on entering being greater than 80°C and the transfer of energy to the gas, the average temperature of the gas in that reaction chamber is brought to 100°C and therefore the thermochemical conversion of sulphur dioxide to partially acidic sulphates and sulphites is reduced.

v) at least an injection chamber provided with means for injecting atomised hydrogen peroxide in solution into the gas in transit to convert the residual sulphur dioxide into sulphuric acid, and to produce ammonium sulphate;

vi) at least a second electrostatic precipitator to retain said ammonium sulphate;

vii) possibly, at least one filtration chamber equipped with bag filters lined with suitable material featuring high specific surface to aid heterogeneous phase chemical reactions in, and improve the removal of the nitrogen oxides from, the gas in transit;

viii) an aspirating-pressing fan positioned upstream of the chimney and functioning at lower pressure than that of the external environment.

The main advantages of the invention are its strong reduction of the ammonia leakage, up to values of less than 1 ppmV (parts per million by volume) and in the removal of more than 99% of the sulphur dioxide.

It is found convenient to detail the invention through an illustration of a plant suitable to implement it and with reference to Fig. 1 wherein:

* a fan 1 that aspirates the gas from a boiler (not shown), in which coal is burnt;
* an exchanger 2 in which the combustion gas reaches temperatures of 140°C-150°C;
* a first cooling chamber 3 in which the gas is cooled to about 110°C by a continuous jet of atomised water 4 obtained by a unit 5 comprising: a source of water 6 and atomisers 7 assisted by compressed air 8 (obviously comprising, a variable flow pump, a regulator valve, a flow meter and valves, not shown);
* a first electrostatic precipitator 9 to remove up to 90% of the light ashes from the gas ;
* a second cooling chamber 10 in which the gas is cooled to about 80°C by a jet of atomised water 11 obtained by means of a unit 12, this also comprising a water source 6' and a source of compressed air 8';
* a reaction chamber 13 constituted by an electrode structure similar to that of an electrostatic precipitator, that is comprising a series of earthed parallel plates (not shown) inter-leaved with a series of frames that carry wires 14 supplied with a positive impulsive voltage from 70 to 100 kV with a repetition frequency of the impulses controllable in the field 30-300 impulses per second to transfer sufficient energy to the gas to remove the required percentage of nitrogen oxides, such reaction chamber being associated with a system 15 suitable for adding dry ammonia to the same chamber and, therefore, comprising a source of ammonia in cylinders, suitable pressure reducers, a regulator valve, "on-off" valves, a device for heating the ammonia, and a source of compressed air to mix the ammonia;
* an injection chamber 16 associated with a source of hydrogen peroxide 17 and a source of compressed air 18 in such a way that by means of a nozzle 19 atomised hydrogen peroxide 20 will be injected into the reaction chamber to convert the sulphur dioxide residue into sulphuric acid that, reacting with the ammonia residue, produces ammonium sulphate;
* a unit of four electrostatic precipitators 21 that retains the ammonia salts, above all the ammonium sulphate that is formed following the removal of the oxide pollutants;
* a bag filter unit 22 associated with a pneumatic system 23 suitable for blowing diatomite onto the external surface of the filters, a source of compressed air 25 to wash the fabric 24;
* an aspirating-pressing fan 26 is fitted into the plant, upstream of a chimney (not shown);
* a control centre 27 to control the course of the entire process in the plant, in particular, according to the method, to control the temperature of the gas in the reaction chambers 13 as a function of the rate of flow of the gas, of the temperature reached by the gas in the cooling chambers, and to control the quantity of the hydrigen peroxide to be injected into the injection chamber.

Claims

1. A method for removing pollutants from a combustion gas wherein there are the phases of:

   a) intaking the gas and cooling it to about 110°C with atomised water in at least a first cooling chamber or in the gas transport duct,

   b) removing up to around 90% of the light ashes present in the gas in at least one first electrostatic precipitator,

   c) further cooling of the gas to bring the temperature to about 80°C,

   d) in at least one reaction chamber, in which

dry ammonia is added to the gas, at the same time energising the gas by means of voltage pulses so as to produce the radicals in the gas and consequently the radical reactions necessary for the removal of part of the nitrogen and sulphur oxides;

and is **characterized** by the subsequent phases of:

maintaining the temperature of the gas in said at least one reaction chamber at about 100°C in order to reduce the thermo-chemical conversion of sulphur dioxide to partially acidic sulphites and sulphates and injecting in at least one injection chamber a solution of hydrogen peroxide into the gas in order to convert the sulphur dioxide residue into sulphuric acid which reacts with the ammonia producing ammonium sulphate, the concentration of hydrogen peroxide in the fumes staying in the region of 0.7 times the concentration of the SO_2 present at the entrance of the plant, and then retaining said ammonium sulphate in at least one second electrostatic precipitator and, possibly, in at least one filtration chamber equipped with suitable filters causing chemical reactions in heterogeneous phase in order to improve the removal of nitrogen oxides.

Patentansprüche

1. Verfahren zum Entfernen von Verunreinigungen aus einem Verbrennungsgas, welches die Phasen umfaßt:

a) Ansaugen des Gases und Kühlen des Gases auf etwa 110°C mit versprühtem Wasser in mindestens einer Kühlkammer oder in dem Gasströmungskanal,
b) Entfernen von bis zu ca. 90% der in dem Gas vorhandenen Flugasche in mindestens einem ersten elektrostatischen Abscheider,
c) weiteres Kühlen des Gases, um die Temperatur auf etwa 80°C zu bringen,
d) in mindestens einer Reaktionskammer, in der trockenes Ammoniak dem Gas zugefügt wird, gleichzeitiges Anregen des Gases durch Spannungsimpulse derart, daß Radikale in dem Gas erzeugt werden und als Folge die für die Entfernung eines Teils der Stickoxide und Schwefeloxide erforderlichen Radikalreaktionen ablaufen;

gekennzeichnet durch die nachfolgenden Phasen:

Halten der Temperatur des Gases in der mindestens einen Reaktionskammer bei etwa 100°C, um die thermochemische Umwandlung von Schwefeldioxid in teilweise saure Sulfite und Sulfate zu reduzieren, und Injizieren einer Lösung von Wasserstoffperoxid in das Gas in mindestens einer Injektionskammer, um den Schwefeldioxidrückstand in Schwefelsaure umzuwandeln, die mit dem Ammoniak zur Bildung von Ammoniumsulfat reagiert, wobei die Konzentration von Wasserstoffperoxid in den Rauchgasen im Bereich des 0,7-fachen der Konzentration des am Einlaß der Anlage vorhandenen SO_2 bleibt, und anschließendes Zurückhalten des Ammoniumsulfats in mindestens einem zweiten elektrostatischen Abscheider und ggf. in mindestens einer Filtrationskammer, die mit geeigneten Filtern versehen ist, zur Bewirkung von chemischen Reaktionen in heterogener Phase, um die Entfernung von Stickoxiden zu verbessern.

Revendications

1. Procédé d'élimination des polluants d'un gaz de combustion, dans lequel il y a les phases de :

a) admission du gaz et son refroidissement jusqu'à environ 110°C avec de l'eau atomisée dans au moins une première chambre de refroidissement ou dans le conduit de transport de gaz ;
b) élimination jusqu'à environ 90 % des cendres légères présentes dans le gaz dans au moins un premier dispositif de précipitation électrostatique ;
c) refroidissement supplémentaire du gaz pour porter la température à environ 80°C ;
d) dans au moins une chambre de réaction dans laquelle de l'ammoniac sec est ajouté au gaz, l'excitation du gaz en même temps à l'aide d'impulsions de voltage, de façon à produire les radicaux dans le gaz et en conséquence les réactions radicalaires nécessaires pour l'élimination d'une partie de l'azote et des oxydes de soufre ;

procédé caractérisé par les phases subséquentes de :

- maintien de la température du gaz dans, au moins, ladite chambre de réaction à environ 100°C, de façon à réduire la conversion thermochimique du dioxyde de soufre en sulfites partiellement acides et sulfates et en injectant dans au moins une chambre d'injection une solution de peroxyde d'hydrogène dans le gaz, de façon à convertir le dioxyde de soufre résiduel en acide sulfurique qui réagit avec l'ammoniac pour produire du sulfate d'ammonium, la concentration du peroxyde d'hydrogène dans les fumées se situant au niveau de

0,7 fois la concentration du SO_2 présent à l'entrée de l'installation, et ensuite en retenant le sulfate d'ammonium dans au moins un second dispositif de précipitation électrostatique et éventuellement dans au moins une chambre de filtration équipée avec des filtres appropriés provoquant des réactions chimiques en phase hétérogène, de façon à améliorer l'élimination des oxydes d'azote.

Fig. 1